

Dynamical Effects and Phase Separation in Thin Films

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We study phase separation in thin films using the Navier–Stokes Cahn–Hilliard equations in the lubrication approximation, modeling substrate–film interactions with a van der Waals potential. We investigate the thin-film equations numerically and compare them with experimental results. We find that the model captures the qualitative features of real phase-separating fluids, in particular the tendency of concentration gradients to produce film thinning and surface roughening. The ultimate outcome of the phase separation depends strongly on the dynamical backreaction of concentration gradients on the flow, as we demonstrate when a shear stress is applied at the film’s surface. When the backreaction is small, the phase domain boundaries align with the direction of the imposed stress, while as the backreaction is made larger, the domains begin to align in the perpendicular direction.

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When a binary fluid is cooled below the critical temperature, the homogeneous state is energetically unfavourable and the system spontaneously phase-separates and forms domains rich in either fluid component [1, 2]. Due to the relevance of phase-separating thin films in industrial applications [3], many experiments and numerical simulations focus on understanding how phase separation is altered if the binary fluid is confined in a thin layer. We propose a lubrication approximation based on the coupled Navier–Stokes Cahn–Hilliard equations to explain the main features of these studies.

Several recent experiments have clarified the different regimes of domain growth in a binary thin film. Wang and Composto [4] have identified early, intermediate, and late stages of evolution. The early stage comprises three-dimensional domain growth, while the intermediate stage is characterized by the formation of wetting layers at the film boundaries, the thinning of the middle layer, and significant surface roughening. Due to the thinning of the middle layer, the sandwich-like structure breaks up and matter from the wetting layer flows back into the bulk. Thus, a late stage is reached, consisting of bubbles coated by thin wetting layers. This characterization of the evolution has been seen in other experiments [5, 6], although clearly a variety of behaviors is possible, depending on the wetting properties of the mixture. Our model captures the essential features of this evolution, in particular the tendency for concentration gradients to promote film rupture and surface roughening.

In a series of papers, Das *et al.* [7, 8] investigate the behaviour of binary fluids with wetting. In [7] they specialize to ultra-thin films. In bulk mixtures, where one of the fluid components is preferentially attracted to the boundary, a layer rich in that component may be established there, followed by depletion layer, and so on. This so-called spinodal wave propagates into the bulk [8]. In

ultra-thin films, the film thickness is less than a single spinodal wavelength and the spinodal wave is suppressed. Two distinct outcomes of phase separation are identified, depending on whether one binary fluid component wets the film boundary completely or partially. Our focus will be on the partially wet case. In this wetting regime, both fluid components are in contact with the film boundaries. The authors find an ultimate state of domain formation extending in the lateral directions and growing in time as $t^{1/3}$, a result that indicates domain growth by Lifshitz–Slyozov diffusion [9].

These papers elucidate the role of wetting and film thickness on the process of phase separation, although they do not discuss hydrodynamics or the effect of free-surface variations on domain formation. In this paper, we therefore focus on ultra-thin films with a variable free surface, and for simplicity we restrict our attention to the case where both fluids experience the same interaction with the substrate and free surface. The model we introduce is based on the Navier–Stokes Cahn–Hilliard (NSCH) equations [10] and gives a qualitative explanation of these studies, in particular the tendency of domain formation to cause film rupture and surface roughening. With an applied external forcing, the model illustrates the salient effect of the dynamical backreaction of concentration gradients on the flow, a useful result in applications where control of phase separation is required [11].

In full generality, the equations we study are

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = \nabla \cdot \mathbf{T} - \frac{1}{\rho} \nabla \phi, \quad (1a)$$

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c = D \nabla^2 (c^3 - c - \gamma \nabla^2 c), \quad (1b)$$

$$\nabla \cdot \mathbf{v} = 0, \quad (1c)$$

where

$$T_{ij} = -\frac{p}{\rho} \delta_{ij} + \nu \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) - \beta \gamma \frac{\partial c}{\partial x_i} \frac{\partial c}{\partial x_j} \quad (1d)$$

is the stress tensor, p is the fluid pressure, ϕ is the body force potential and ρ is the constant density. Addition-

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ally, ν is the kinematic viscosity, β is the mixture free energy per unit mass, D is the Cahn–Hilliard diffusion coefficient, and $\sqrt{\gamma}$ is the thickness of domain boundaries. The concentration boundary condition for Eq. (1) is $\mathbf{n} \cdot \nabla c = \mathbf{n} \cdot \nabla (c^3 - c - \gamma \nabla^2 c) = 0$, where \mathbf{n} is a vector normal to the boundary, while the velocity boundary conditions on the velocity and stress tensor are standard [12]. We nondimensionalize these equations by using the vertical length scale h_0 , the horizontal or lateral length scale λ , and the diffusion time λ^2/D . If the parameter $\varepsilon = h_0/\lambda$ is small, a lubrication approximation is possible [12]. We take the following dimensionless groups to be of order unity,

$$Re = \frac{\varepsilon D}{\nu}, \quad C = \frac{D}{\varepsilon^2 h_0^2 \sigma_0 \rho \nu},$$

$$r = \frac{\varepsilon^2 \beta \gamma}{D \nu}, \quad C_n = \frac{\varepsilon \sqrt{\gamma}}{h_0},$$

where Re is the Reynolds number, C_n is the Cahn number [10] which provides a dimensionless measure of domain wall thickness, r is a dimensionless measure of the backreaction strength, and C^{-1} is a dimensionless measure of surface tension corresponding to the dimensional surface tension σ_0 . Using these scalings, we expand the nondimensional version of Eq. (1) in powers of ε , following the method outlined in [12], and obtain equations for the free surface height $h(x, y, t)$ and concentration $c(x, y, t)$,

$$\frac{\partial h}{\partial t} + \nabla_\perp \cdot (\mathbf{u}h) = 0, \quad (2a)$$

$$\frac{\partial}{\partial t} (ch) + \nabla_\perp \cdot (\mathbf{u}ch) = \nabla_\perp \cdot (h \nabla_\perp \mu), \quad (2b)$$

where

$$\mathbf{u} = \frac{1}{2} h \nabla_\perp \sigma - \frac{1}{3} h^2 \nabla_\perp p,$$

$$p = -\frac{1}{C} \nabla_\perp^2 h + \phi(x, y, h(x, y, t)) + r (\nabla_\perp c)^2,$$

$$\mu = c^3 - c - C_n^2 \frac{1}{h} \nabla_\perp \cdot (h \nabla_\perp c).$$

Here $\nabla_\perp = (\partial_x, \partial_y)$ is the gradient operator in the lateral directions, σ is the surface tension, ϕ is the body force potential, \mathbf{u} is a vertically-averaged velocity, p as a vertically-averaged pressure, and μ as the chemical potential. While the equations do not allow for vertical variations in concentration, we show in what follows that the model reproduces the qualitative features observed in thin binary fluids, especially in the case where both binary fluid components interact identically with the substrate and free surface [7].

For thin films with $h_0 = 100\text{--}1000$ nm [4, 5], the dominant contribution to the potential is due to van der Waals interactions [12, 13], and following these authors we take $\phi = A/h^3$, where A is the dimensionless Hamaker coefficient. To prevent rupture [12], we study films where $A < 0$, and take A to be independent of

the concentration level, so that both binary fluid components are attracted equally to the substrate and free surface boundaries. In this case, Eq. (2) possesses simple one-dimensional equilibrium solutions, obtained by setting $\mathbf{u} = \nabla_\perp \mu = 0$. From Fig. 1 we see that the one-

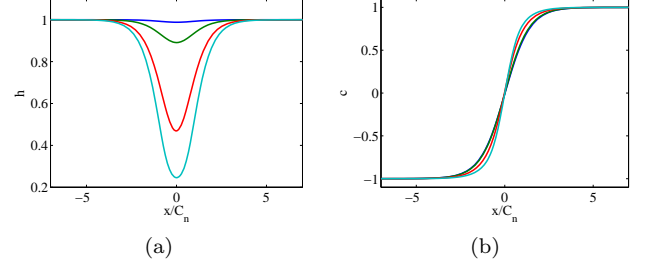


FIG. 1: (Color online) Equilibrium solutions of Eq. (2) for $C = C_n^2 = |A| = 1$ and $r = 0.1, 1, 10, 50$. In (a) the valley deepens with increasing r although the film never ruptures, while in (b) the front steepens with increasing r .

dimensional equilibrium solution of Eq. (2), with boundary conditions $h(\pm\infty) = 1$, $c(\pm\infty) = \pm 1$, consists of a step-like profile for the concentration, corresponding to a pair of domains separated by a smooth transition region. Across this transition region, the height field dips into a valley. While the valley increases in depth for large backreaction strength r , the film never ruptures. This result follows from the inequality $h''(0) > 0$, since $x = 0$ is a local minimum. Thus, from the equilibrium condition $u = 0$,

$$0 < \left[1 + \frac{r}{|A|} c'(0)^2 \right]^{-1} < [h(0)]^3.$$

In this way, the repulsive van der Waals potential has a regularizing effect on the solutions.

Physically, the formation of the valley arises from the balance between the van der Waals and backreaction effects. From the solution in Fig. 1, the capillary force $F_{\text{cap}} = -r \partial_x (\partial_x c)^2$ and the van der Waals force $F_{\text{vdW}} = |A| \partial_x h^{-3}$ always have opposite sign. The repulsive van der Waals force acts as a non-linear diffusion [14] and inhibits rupture, and therefore F_{cap} promotes rupture, a result seen in experiments [4]. The valley in the height field represents a balance between the smoothening and the rupture-inducing effects.

As in ordinary Cahn–Hilliard dynamics [2], the one-dimensional equilibrium solution hints at the late-time configuration in higher dimensions. Thus, we expect the multidimensional solution to comprise concentration domains with a height field of peaks and valleys, with valleys occurring at domain boundaries. We have verified with numerical simulations that this is indeed the case. By using a measure of domain size (L_x, L_y) based on the Fourier transform of the correlation function $\langle c(\mathbf{x}, t) c(\mathbf{x} + \mathbf{r}, t) \rangle$ [15], we have found that the domains grow in time as $t^{1/3}$, the usual Lifshitz-Slyozov

growth law [9]. Here $\mathbf{x} = (x, y)$ denotes the lateral coordinates and $\langle \dots \rangle$ denotes the spatial average. The modified growth exponent due to hydrodynamic effects [2, 16] is not observed, a result that emerges from the non-linear diffusive character of the height equation, which damps any undulations not caused by concentration gradients. The surface roughness arising from the concentration gradients is similar to that observed in the one-dimensional case and has been seen in several experiments [4, 17].

The dramatic effect of the reaction of the concentration gradients on the phase separation is apparent when we apply a surface tension gradient across the film. Physically, this can be realized by differential heating of the surface [18], although a surfactant will also induce stresses at the surface [19]. We set $\sigma = \sigma_0 \sin kx$, where $k = (2\pi/L)m = k_0 m$ is the spatial scale of the surface tension variation and m is an integer. Then the velocity that drives the system becomes

$$\mathbf{u} = \frac{1}{2}h(k\sigma_0 \cos kx, 0) + \frac{1}{3}h^2 \nabla_{\perp} \left[\frac{1}{C} \nabla_{\perp}^2 h + \frac{|A|}{h^3} - r(\nabla_{\perp} c)^2 \right]. \quad (3)$$

This velocity field may also be obtained by imposing a shear stress $\boldsymbol{\tau}$ at the surface, provided $\boldsymbol{\tau} = \nabla \sigma$ [20]. We carry out simulations using Eq. (3) on a 128×128 grid. The results do not change upon increasing the resolution. We choose C_n so that domain boundaries are resolved. The other parameter values are indicated in the caption to Fig. 2.

This choice of velocity field leads to control of phase separation in the following manner. For small values of the backreaction strength, with $r \rightarrow 0$, the height field

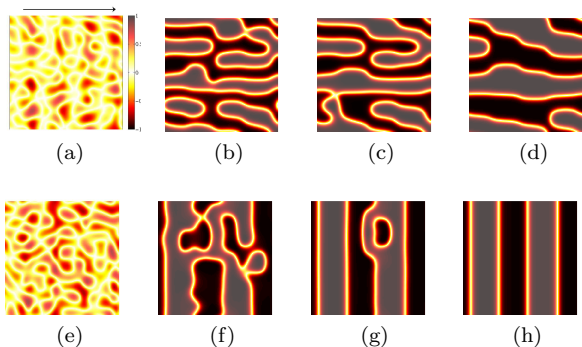


FIG. 2: (Color online) The concentration field for $C = -A = 1$. Across the first row, $r = 0$ and (a) $t = 500$; (b) $t = 3750$; (c) $t = 7500$; (d) $t = 30000$. Across the second row, $r = \frac{1}{2}$ and (e) $t = 500$; (f) $t = 3750$; (g) $t = 7500$; (h) $t = 30000$. The surface tension gradient is parallel to the arrow and $\sigma = \sigma_0 \sin(kx)$, $\sigma_0 = 20$ and $k = 4k_0$. In Figs. (a)–(d) with $r = 0$, the domains align along the arrow, while in Figs. (e)–(h) with moderate backreaction strength, the domains align in a direction perpendicular to the arrow.

quickly aligns with the surface tension profile as in Fig. 3, since the strong effect of the van der Waals diffusion destroys the unforced part of $h(\mathbf{x}, t)$. At the same time,

the concentration field begins to form domains. At later times, when $L_x(t), L_y(t) \sim 2\pi/k$, the domains align with the gradient of the forcing term. The growth of the domains continues in this direction and is arrested (or slowed down considerably) in the direction perpendicular to the forcing. The domains are string-like, with kinks occurring along lines where $\sigma(x, y)$ is minimized, as evidenced by Fig. 2 (a)–(d). The growth of L_x and L_y is shown in Fig. 4. It is not clear whether L_y is arrested or undergoes slow linear growth and so we do not report its growth rate.

For moderate values of the backreaction strength with $r \sim O(1)$, the height field again assumes a profile aligned with the surface tension, while domains of concentration now align in a direction perpendicular to the forcing gra-

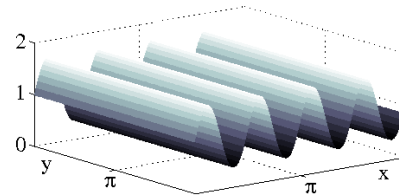


FIG. 3: The height field for $r = 0$ and $t = 30000$ aligns with the applied surface tension. The height field at $t = 30000$ for $r = \frac{1}{2}$ is similar.

dient. Domain growth continues in the perpendicular direction and is arrested in the direction of the driving-force gradient. A pattern of string-like domains emerges, with domain boundaries forming along lines where both $\sigma(x, y)$ and $h(x, y, t)$ are maximized. Eventually, the domain boundaries align perfectly with the surface tension maxima, as evidenced in Fig. 2 (e)–(h).

The control of phase separation by surface shear therefore depends crucially on the backreaction. This result is amplified by the existence of a no-rupture condition only for the $r = 0$ case (no backreaction). This condition relies on the alignment of the height and surface tension profiles, which is exact only when the backreaction is zero. Then, at late times, the system evolves towards equilibrium and is described by the steady state $\nabla_{\perp} \cdot (\frac{1}{2}h^2 \nabla_{\perp} \sigma - \frac{1}{3}h^3 \nabla_{\perp} p) = 0$, which by the alignment property reduces to the one-dimensional equation

$$h^2 \left[\frac{1}{2} \frac{d\sigma}{dx} + \frac{1}{3} h \frac{d}{dx} \left(\frac{1}{C} \frac{d^2 h}{dx^2} + \frac{|A|}{h^3} \right) \right] = \text{const.}$$

By multiplying both sides of the expression by h , differentiating and then evaluating the result at x_0 , a minimum of both surface tension and height, we obtain the condition

$$[h(x_0)]^3 \left[\frac{1}{3C} h(x_0) h^{(4)}(x_0) + \frac{1}{2} k^2 \sigma_0 \right] = |A| h''(x_0). \quad (4)$$

Since x_0 is a minimum of height, $h''(x_0) > 0$, which prevents $h(x_0)$ from being zero. On the other hand, for

r and σ_0 sufficiently large, the alignment of height and surface tension profiles is not exact, the one-dimensional state is never reached and hence the result in Eq. (4) does not apply. In that case, simulations show that the film ruptures in finite time.

Given an applied surface tension gradient, we have outlined, by numerical simulations and calculations, three possible outcomes for the phase separation, depending on

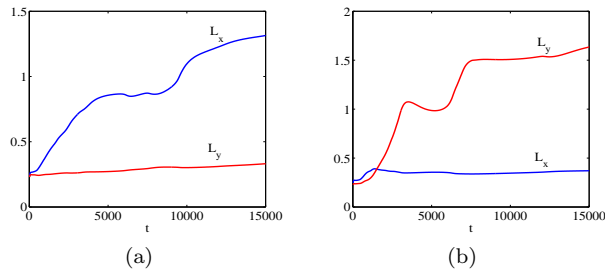


FIG. 4: (Color online) Growth of L_x and L_y for (a) $r = 0$, where L_x grows and L_y saturates or undergoes slow growth. Since the growth rate of L_y is small, it is not clear whether saturation or slow linear growth takes place; (b) $r = \frac{1}{2}$, where L_x saturates and L_y grows.

the backreaction strength r . For $r \ll 1$, the concentration forms string-like domains, aligned with the applied force. For $r \sim O(1)$, the concentration forms domains that align perfectly in a direction perpendicular to the applied force. For $r \gg 1$, the forcing causes the film to rupture. The interfacial tension or backreaction must therefore be chosen carefully in a real fluid to achieve the

desired outcome.

In conclusion, we have derived a thin-film model of phase separation based on the Navier–Stokes Cahn–Hilliard equations, in which the reaction of concentration gradients on the flow is important. We have used this model to give a qualitative picture of the features of phase separation in real thin films, in particular the tendency of concentration gradients to promote rupture in the film, and to produce peaks and valleys in the free surface that mirror the underlying domain morphology. We have found that in the presence of a unidirectional sinusoidal variation in surface tension, the strength of the backreaction determines the direction in which the domains align. This result could prove useful in microfabrication applications where control of phase separation is required [11].

Because the lubrication model suppresses vertical variations in the concentration field, we are limited to the case where the binary fluid components interact identically with the boundaries at the substrate and free surface. However, the model quite generally gives an accurate description of surface roughening arising from van der Waals forces. More detailed models based on this approach, involving different boundary conditions that better reflect wetting behaviour [7, 21] and a concentration-dependent Hamaker coefficient, will capture a wider range of thin-film behaviour.

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